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van Piggelen, H. U.; Nieuwpoort, W. C.; van der Velde, G. A.

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Gaussian basis sets for the rare earths

H. U. van Piggelen, W. C. Nieuwpoort, and G. A. van der Velde

Department of Chemical Physics, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

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Extended Gaussian basis sets have been calculated for the neutral and trivalent rare earth atoms. The characteristics of these sets, which are available on request, are reported. The quality of the wave functions is discussed on the basis of a comparison of a number of calculated properties with those of numerical Hartree-Fock calculations. The agreement shown is very satisfactory.

INTRODUCTION

Recently we have started an investigation of the electronic structure of rare earth compounds by means of *ab initio* self-consistent-field calculations. These calculations were carried out in the framework of the Hartree-Fock-Roothaan formalism employing a basis set of Gaussian-type orbitals. Satisfactory basis sets of this type have been published for many atoms¹⁻⁶ but, as far as we are aware, not for the rare earths. We have therefore determined such sets for the neutral rare earth atoms and their trivalent ions. The purpose of the present paper is twofold. First we want to draw the attention of theoretical workers in this field to the existence of these basis sets and to the fact that a limited number of copies can be obtained from the authors on request. Second, a brief description is presented of the main characteristics of the sets, including an assessment of their quality by means of a comparison with numerical Hartree-Fock results.

BASIS SET SIZE

The size of the basis sets was determined by requiring on the one hand very good agreement between various atomic properties calculated with these sets and the corresponding properties resulting from numerical Hartree-Fock (NHF) calculations. On the other hand they should still be manageable in molecular calculations to be carried out later. For the trivalent ions these requirements resulted in sets consisting of 18s, 15p, 10d, and 8f type functions. For the neutral atoms three s-type functions had to be added, two of which were mainly used to describe the outer part of the 6s orbital. These sets are hence quite large and we could use them in our molecular calculations only by applying contraction and by making use of the high molecular symmetry of the calculated compounds.⁸

There are a number of reasons for insisting on basis sets of this size. First, their ability of reproducing numerical Hartree-Fock results closely is a desirable feature. The chances of producing artefacts in the results of molecular calculations due to basis set deficiencies are hereby considerably reduced. Second, since these basis sets not only describe the valence regions of the atomic wave functions well but also their core regions, inner shell properties can be studied as well. Detailed comparison between quantities calculated respectively by Hartree-Fock and Fock-Dirac wave functions⁹ seems to indicate that in general the changes oc-

curing in atomic orbitals due to relativistic effects should not be neglected, as we have done, in molecular calculations. Whether this is achieved by setting up and solving Fock-Dirac equations for molecules¹⁰ or by adding relativistic correction operators to the nonrelativistic Hamiltonian,¹¹ a Gaussian basis set will be necessary. The sets presented here are probably flexible enough to be of direct use in such calculations also. Alternatively they should provide a very good starting point for finding optimal relativistic basis sets.

The exponents were determined by an atomic optimi-

TABLE I. Exponents and contraction coefficients for the 18/15/10/8 basis of $\text{Eu}^{3+}({}^7F)$.

Exponent	Contraction coefficient	Exponent	Contraction coefficient
s orbitals		p orbitals	
0.73316845 E+7	0.000410	0.45245367 E+5	0.000209
0.11142983 E+7	0.000312	0.10724683 E+5	0.001838
0.25622389 E+6	0.001618	0.34832046 E+4	0.010307
0.73271281 E+5	0.006693	0.13306175 E+4	0.042846
0.24142462 E+5	0.023418	0.56338984 E+3	0.133927
0.88207490 E+4	0.070162	0.25583379 E+3	0.296197
0.34879268 E+4	0.174296	0.12202964 E+3	0.398043
0.14651388 E+4	1.0	0.60004889 E+2	1.0
0.64718566 E+3	0.232039	0.29023320 E+2	0.456281
0.29855763 E+3	0.101025	0.14570416 E+2	0.534294
0.12310029 E+3	1.0	0.69292812 E+1	1.0
0.57024535 E+2	1.0	0.33700100 E+1	1.0
0.22199572 E+2	1.0	0.15841663 E+1	1.0
0.11696707 E+2	1.0	0.65708044 E+0	1.0
0.45229296 E+1	1.0	0.27499552 E+0	1.0
0.22556381 E+1	1.0		
0.63233382 E+0	1.0		
0.29762918 E+0	1.0		
(0.4849151 E-1)			
(0.2068146 E-1)			
d orbitals		f orbitals	
0.20270637 E+4	0.001056	0.18745106 E+3	0.002883
0.61212917 E+3	0.009742	0.64340367 E+2	0.022503
0.23797407 E+3	0.050175	0.26700765 E+2	0.087177
0.10429623 E+3	0.165762	0.12001284 E+2	0.216523
0.48924891 E+2	0.340726	0.55610916 E+1	0.340681
0.23762016 E+2	0.407395	0.25428702 E+1	0.355607
0.11725089 E+2	1.0	0.11107292 E+1	0.365607
0.56554877 E+1	1.0	0.44298548 E+0	1.0
0.26328807 E+1	1.0		
0.11204504 E+1	1.0		

TABLE II. Calculated total energies and spin-orbit coupling constants for trivalent rare earth ions (18/15/10/8). Ground state multiplets from Ref. 16.

Ion	Term	Configuration	Total energy (a.u.)		$\zeta(4f)$ (cm ⁻¹)	
			This work	NHF	This work	NHF
Ce	² F	4f ¹	-8565.6198	-8565.640	777.3	778.2
Pr	³ H	4f ²	-8919.8159	-8919.832	917.8	918.6
Nd	⁴ I	4f ³	-9282.5028	-9282.515	1063.3	1064.1
Pm	⁵ I	4f ⁴	-9653.7074	-9653.721	1215.3	1216.2
Sm	⁶ H	4f ⁵	-10033.5027	-10033.521	1377.3	1378.3
Eu	⁷ H	4f ⁶	-10422.0169	-10422.028	1554.3	1555.4
Gd	⁸ S	4f ⁷	-10819.3505	-10819.372	1747.2	1748.4
Tb	⁷ F	4f ⁸	-11225.2170	-11225.234	1939.9	1941.3
Dy	⁶ H	4f ⁹	-11640.0427	-11640.061	2151.7	2153.2
Ho	⁵ I	4f ¹⁰	-12063.8812	-12063.902	2381.2	2382.9
Er	⁴ I	4f ¹¹	-12496.7472	-12496.767	2626.6	2628.4
Tm	³ H	4f ¹²	-12938.7124	-12938.739	2888.7	2890.6
Yb	² F	4f ¹³	-13389.9176	-13389.945	3169.9	3172.0

TABLE III. Calculated total energies and spin-orbit coupling constants for neutral rare earth atoms (21/15/10/8). Ground state multiplets from Ref. 16.

Atom	Configuration	Term	Total energy (a.u.)		$\zeta(4f)$ (cm ⁻¹)	
			This work	NHF	This work	NHF
Ce	4f ¹ 5d ¹	¹ G	-8566.8471	-8566.880	747.7	749.2
Pr	4f ³	⁴ I	-8921.1725	-8921.190	819.2	820.1
Nd	4f ⁴	⁵ I	-9283.8739	-9283.887	956.5	957.5
Pm	4f ⁵	⁶ H	-9655.0895	-9655.105	1102.4	1103.4
Sm	4f ⁶	⁷ F	-10034.9426	-10034.957	1261.9	1263.0
Eu	4f ⁷	⁸ S	-10423.5324	-10423.543	1436.2	1437.5
Gd	4f ⁷ 5d ¹	⁹ D	-10820.6269	-10820.663	1734.4	1736.2
Tb	4f ⁸	⁶ H	-11226.5565	-11226.575	1800.4	1802.0
Dy	4f ¹⁰	⁵ I	-11641.4398	-11641.456	2008.3	2010.0
Ho	4f ¹¹	⁴ I	-12065.2765	-12065.298	2231.0	2232.9
Er	4f ¹²	³ H	-12498.1383	-12498.146	2469.4	2471.5
Tm	4f ¹³	² F	-12940.1594	-12940.186	2726.0	2728.3
Yb	4f ¹⁴	¹ S	-13391.4403	-13391.459

TABLE IV. Various one-electron expectation values for Eu³⁺ (⁷F).

nl	-ε (a.u.)		⟨r⟩ (a.u.)		⟨r ⁴ ⟩ (a.u.)	
	This work	(NHF)	This work	(NHF)	This work	(NHF)
1s	1691.891	1691.892	0.024081	0.024081	0.000002	0.000002
2s	273.541	273.541	0.102526	0.102526	0.000258	0.000257
3s	62.572	62.573	0.264422	0.264422	0.009544	0.009536
4s	13.969	13.969	0.597854	0.597854	0.234487	0.234334
5s	2.839	2.839	1.452698	1.452850	8.088262	8.114354
2p	259.583	259.578	0.087115	0.087115	0.000165	0.000165
3p	56.333	56.333	0.254550	0.254550	0.008801	0.008800
4p	11.464	11.464	0.613383	0.613372	0.271015	0.270996
5p	2.051	2.051	1.606312	1.606753	12.519212	12.598712
3d	44.855	44.855	0.226536	0.226536	0.006417	0.006417
4d	6.975	6.975	0.653079	0.653124	0.393401	0.394333
4f	1.885	1.885	0.806246	0.806439	1.474691	1.489782

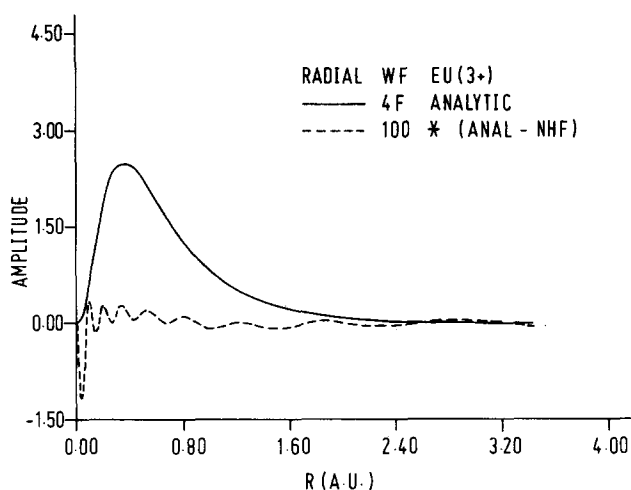


FIG. 1. Plot of logarithm of orbital exponents of $\text{Eu}^{3+}(4f)$ basis.

zation program written by one of us (v.d.V.). With this program the total SCF energy of an atom or ion can be minimized with respect to simultaneous variations in the orbital exponents. The optimization method used, is that of Davidson-Fletcher-Powell.⁷

RESULTS AND DISCUSSION

By way of example, Table I displays the exponents for Eu^{3+} together with the contraction coefficients that define the contracted basis functions which have been used in our calculations on $(\text{EuO}_6)^{9-}$.⁹ The same contraction scheme, leading to a reduced basis set of 12s-, 9p-, 6d-, and 2f-type functions can be used for the other ions. It should be noted that in this table the exponents that describe the outer part of the 6s orbital in the neutral atom have been added in parentheses.

The total energies and the spin-orbit coupling constant $\zeta(4f)$, calculated according to the Blume-Watson formulas,¹² respectively with our basis sets and the NHF program¹³ are compared in Tables II and III. The agreement shown is very satisfactory. The differences in the total energies are generally smaller than 0.03 a.u. and appear to a large extent systematically in all states of a particular atom. Calculated energy differences such as ionization energies therefore are essentially the same for the two methods of computation. Table IV finally allows a comparison between various one-electron properties for the Eu^{3+} ion. The agreement is again satisfactory and is representative for the results obtained for the other ions. We note that the expectation values of r^n show increasing deviations when n gets larger, particularly for the outer orbitals 5s, 5p, and 4f. This is indicative of the relatively poor representation of the tail parts of these functions. In Fig. 1 the radial 4f function obtained with our basis set is plotted. The dotted line represents the difference between this function and the NHF function, which had to be multiplied by 100 to make it visible. The figure indicates that it is difficult to represent the inner parts of atomic orbitals with Gaussian functions. It may be

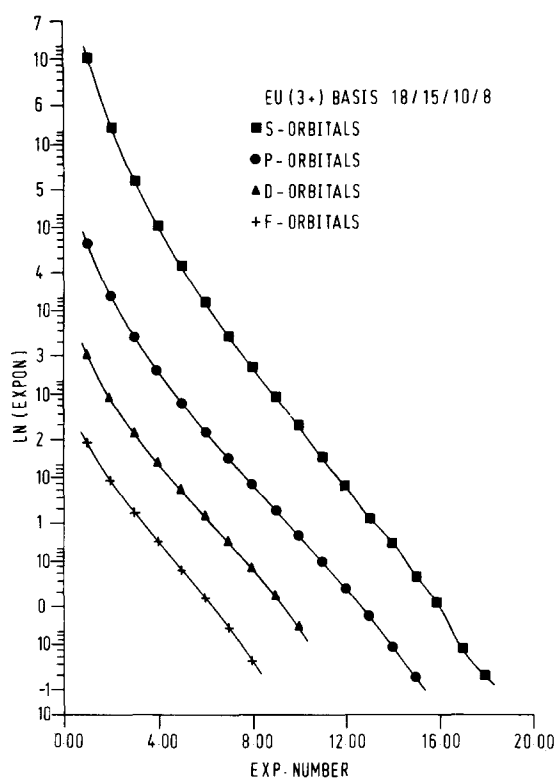


FIG. 2. Plot of 4f orbital in $\text{Eu}^{3+}(4f)$ (solid line), dotted line: 100 times the difference between analytical and NHF orbital.

noted, however, that earlier work on the Mössbauer isomer shifts in iron compounds¹⁴ has demonstrated the usefulness of Gaussian basis sets in this region as well. Finally, in Fig. 2 the logarithm of the orbital exponents of the Eu^{3+} basis functions is plotted against their count number. The approximate linear behavior especially for the lower exponents is observed for the other ions as well. This is a feature which we have found to be useful in molecular calculations when one wants to add some more functions with more diffuse exponents to the basis set.¹⁵

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